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(54) **Oil additive concentrates and lubricants of enhanced performance capabilities**

Öladditivkonzentrate und Schmieröle mit verbesserten Leistungen

Concentrés d'additifs pour huile et lubrifiants aux performances améliorées

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• Sieberth John, F.  
Baton Rouge, Louisiana 70815 (US)

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(74) Representative: **Woods, Geoffrey Corlett et al**  
**J.A. KEMP & CO.**  
14 South Square  
Gray's Inn  
London WC1R 5LX (GB)

(73) Proprietor: **ETHYL PETROLEUM ADDITIVES  
LIMITED**  
Bracknell, Berkshire RG12 2UW (GB)

(72) Inventors:  
• MacPherson, Ian  
Berkshire SL6 OLD (GB)

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**EP-A- 430 624** **EP-A- 459 656**  
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**EP 0 531 585 B1**

## Description

This invention relates to additive concentrates and oleaginous compositions (e.g., lubricating oils and functional fluids) having enhanced performance properties.

Heretofore a number of additive concentrates containing, inter alia, sulphur-containing antiwear and/or extreme pressure additives, phosphorus-containing antiwear and/or extreme pressure additives, and other additive components have been proposed and used. Among such other additive components are acidic components such as carboxylic acids, hydrocarbyl phosphoric acids, and hydrocarbyl thiophosphoric acids; basic components such as amines; and ashless dispersants such as boronated succinimides.

The quality of automotive gear oils can be assessed by evaluating their performance in a number of tests. There are many tests which can be used to evaluate the antiwear, extreme pressure, oxidation, corrosion, etc., properties of the oil.

The American Petroleum Institute, API, has established a well known series of service designations, each of these designations referring to the performance requirements of a gear lubricant for a specific type of automotive service. API GL-5 is one such designated classification which particularly relates to hypoid gears and other automotive equipment which may be operated under high-speed, shock-load; high-speed, low-torque; and low-speed, high-torque conditions. In order to assess the suitability of a lubricant for an API GL-5 classification, the oil must pass certain performance tests. One of these tests, CRC L-60, examines the oxidative stability of a lubricant when subjected to extreme oxidative and thermal conditions.

One further facet of the CRC L-60 test, which is not part of API GL-5, is that the test may also be used to assess the deposit forming characteristics of the lubricant. Any sludge or/and varnish which is deposited on the gear faces during the test may be rated by an industry established procedure as a numerical rating from 1 to 10. A rating of 1 is very high sludge and/or varnish whilst 10 is no sludge or varnish.

This invention relates in part to the control of deposits in the CRC L-60 oxidation stability test using additive systems capable of providing good antiwear and/or extreme pressure performance. Thus one objective of this invention is to fulfill these requirements.

There is, additionally, a need for automotive gear oil formulations which not only meet GL-4 and/or GL-5 requirements but which afford superior results in a planetary spur gear test referred to hereinafter.

Still another need is for an ashless or low-ash lubricant additive package affording high dispersancy and high wear resistance to lubricants, such as crankcase lubricants, gear lubricants, manual and automatic transmission fluids, oil-based hydraulic fluids, wet brake fluids, and similar lubricants and functional fluids.

Yet another need is for an automotive or industrial gear oil package which performs well in synthetic base oils.

In accordance with one embodiment of this invention, there is provided an additive concentrate which comprises the following oil-soluble components:

- a) a boronated Mannich base ashless dispersant;
- b) a metal-free sulphur-containing antiwear and/or extreme pressure agent;
- c) a metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
- d) an oil-soluble amine salt of a carboxylic acid.

Another embodiment of this invention involves the provision of an additive concentrate which comprises a diluent oil and at least 20% by weight, and preferably at least 50% by weight, of additive components a), b) and c) such that the mass ratio (wt/wt) of nitrogen in the boronated Mannich base dispersant a) to sulphur in the sulphur-containing antiwear and/or extreme pressure agent b) is in the range of 0.0005:1 to 0.5:1, and preferably in the range of 0.003:1 to 0.2:1.

Still another embodiment of this invention comprises an additive concentrate which comprises a diluent oil and at least 20% by weight, and preferably at least 50% by weight, of additive components a), b) and c) such that the mass ratio (wt/wt) of nitrogen in the boronated Mannich base dispersant a) to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent c) is in the range of 0.005:1 to 5:1, and preferably in the range of 0.01:1 to 2:1.

In additional preferred embodiments, any of the above additive concentrates further comprise at least one oil-soluble demulsifying agent.

In still other preferred embodiments, any of the above additive concentrates further comprise at least one oil-soluble amine salt of a sulphur-free hydrocarbyl phosphoric acid.

Other preferred embodiments of this invention involve the provision of additive concentrates of the type described above wherein the pH of such concentrates, when measured by the method described below, falls in the range of 3 to 10 and more preferably in the range of 6 to 8. In a strict sense, such concentrates do not have a classical pH inasmuch as they consist essentially of a solution of various organic compounds, usually in an oil, typically a hydrocarbon oil.

Nevertheless, when a sample of such concentrates is dissolved in a mixture of methanol and toluene, it is possible to assay the sample with a conventional pH probe of the type used in aqueous systems. This provides a useful measure of the relative proportions of basic and acidic materials present in the composition. A detailed procedure for conducting such pH measurements is set forth hereinafter.

In particularly preferred embodiments, any of the foregoing additive concentrates further comprise at least one oil-soluble amine salt of a carboxylic acid, and optionally free amine.

Also provided by this invention are lubricant compositions which comprise a major proportion of at least one oil of lubricating viscosity and a minor amount of the various additive combinations referred to hereinabove.

In an embodiment of the invention, a) comprises a boronated Mannich base ashless dispersant formed by reacting a long chain hydrocarbon-substituted phenol with formaldehyde and a polyalkylene polyamine, and boronating the resultant condensation product, component b) comprises sulphurised isobutylene, component c) comprises an amine salt of a monohydrocarbyl and/or dihydrocarbyl ester of a phosphoric and/or monothiophosphoric acid, and component d) comprises a tertiary alkyl primary monoamine salt of an aliphatic monocarboxylic acid. In this embodiment the amine of components c) and d) typically comprises a tert-alkyl primary monoamine in which the alkyl group contains at least 10 carbon atoms.

Still other especially preferred embodiments of this invention are the following:

A) An additive concentrate which comprises one or more of each of the following oil-soluble additive components:

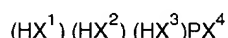
- a) a boronated Mannich base ashless dispersant;
- b) a metal-free sulphur-containing antiwear and/or extreme pressure agent;
- c) a metal-free phosphorus-containing and nitrogen-containing antiwear and/or extreme pressure agent; and
- d) an oil-soluble amine salt of a carboxylic acid; and
- e) optionally, free amine. When used, the free amine is preferably used in an amount sufficient to render the pH of the concentrate, when measured in accordance with the method described hereinafter, in the range of 6 to 8.

B) A concentrate as in A) further comprising at least one oil-soluble trihydrocarbyl ester of a dithiophosphoric acid.

C) A concentrate as in A) or B) further comprising at least one oil-soluble demulsifying agent.

D) A concentrate as in any of A) through C) further comprising at least one oil-soluble copper corrosion inhibitor.

E) A concentrate as in any of A) through D) in which component c) comprises (i) at least one oil-soluble amine salt of a monohydrocarbyl and/or dihydrocarbyl ester of a phosphoric or thiophosphoric acid, such acid having the formula



wherein each of  $X^1$ ,  $X^2$ ,  $X^3$  and  $X^4$  is, independently, an oxygen atom or a sulphur atom, and most preferably wherein at least three of them are oxygen atoms; (ii) at least one oil-soluble phosphorus- and nitrogen-containing composition formed by reacting a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide to produce an acidic intermediate, and neutralizing a substantial portion of said acidic intermediate with at least one amine or hydroxy amine; (iii) at least one oil-soluble amine salt of a hydroxy-substituted phosphetane or a hydroxy-thiophosphetane (sometimes referred to as "phosphetans" or "thiophosphetans"); or a combination of any two or all three of (i), (ii) and (iii).

F) A concentrate as in any A) through E) in which component b) comprises at least one sulphurized olefin.

G) A concentrate as in any of A) through F) in which component c) comprises a combination of (i) one or more monoalkyl or monoalkenyl monoamine salts of a mono- or dihydrocarbyl ester of phosphoric acid, and (ii) one or more monoalkyl or monoalkenyl monoamine salts of a mono- or dihydrocarbyl ester of at least one monothiophosphoric acid.

H) A concentrate as in any of A) through G) in which component d) comprises one or more monoalkyl or monoalkenyl monoamine salts of at least one alkanolic or alkenolic acid.

I) A concentrate as in any of A) through H) in which component e) comprises one or more monoalkyl or monoalkenyl monoamines.

J) A concentrate as in any of A) through I) in which: (i) component a) comprises at least one boronated Mannich base ashless dispersant formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to 2.5 moles of formaldehyde and from about 0.5 to 2 moles of polyalkylene polyamine, and by boronating the resultant condensation product; (ii) component b) comprises sulphurized isobutylene; (iii) the ester of phosphoric acid and the ester of monothiophosphoric acid of component c) comprise alkyl esters in

which the alkyl groups may be the same or different and contain in the range of from 4 to 12 carbon atoms each; (iv) the amine of components c), d), and e) comprises a mixture of C<sub>12</sub> to C<sub>14</sub> tertiary alkyl primary monoamines; and (v) the acid of component d) comprises oleic acid.

K) A concentrate as in any of A) through J) wherein the pH of the concentrate, when measured in accordance with the method described hereinafter, as in the range of 4 to 10.

L) An oleaginous composition which comprises at least one oil of lubricating viscosity containing at least the oil-soluble additive components in accordance with any one of A) through K).

M) A method of lubricating relatively moving metallic surfaces in close proximity to each other which comprises providing for use or using as the lubricant for such surfaces an oleaginous composition which comprises at least one oil of lubricating viscosity containing at least the oil-soluble additive components in accordance with any one of A) through K). Typically, the relatively moving metallic surfaces comprise surfaces of at least two interacting metallic gears that transfer mechanical energy during operation.

N) Apparatus comprising (i) metallic mechanical parts in close proximity to each other requiring lubrication, such as apparatus comprising at least two interacting metallic gears that transfer mechanical energy during operation, and (ii) as a lubricant therefor, at least one oil of lubricating viscosity containing at least the oil-soluble additive components in accordance with any one of A) through K).

Preferably, the finished lubricant compositions of this invention are ashless or low-ash compositions, that is, they contain at most 100 parts by weight of metal introduced as one or more additive components per million parts by weight of base oil ("ppm"), preferably no more than 50 ppm of metal, and most preferably zero to at most 25 ppm of metal introduced as one or more additive components. Accordingly, the additive concentrates of this invention are preferably proportioned such that if one or more metal-containing components (e.g., zinc dihydrocarbyldithiophosphate and/or metal detergent) are included therein, the additive concentrate when employed in a base oil at the selected or recommended dosage level will yield a finished lubricant having at most 100 ppm, preferably at most 50 ppm, and more preferably at most 25 ppm of added metal. Compositions devoid of added metal content are most especially preferred. In this connection, neither boron nor phosphorus is subject to these preferred limitations on metal content, as neither such element is a metal. Thus the mere fact that boron and/or phosphorus components may leave residues during usage, is of no relevance as regards these preferred limitations on metal content.

The additive combinations of this invention have the capability of contributing greatly improved performance properties to base oils of lubricating viscosity, including animal, vegetable, mineral, and synthetic oils. For example, significantly improved properties can be achieved in lubricant compositions of this invention when subjected to various API GL-5 test procedures, such as enhanced extreme pressure properties as seen in the standard CRC L-42 test, improved antirust performance as seen in the standard CRC L-33 test, and/or clean gears as seen in the standard CRC L-60 test. Indeed, particularly preferred compositions of this invention are those which satisfy all of the requirements of the API GL-5 test procedures. In addition, particularly preferred compositions of this invention exhibit superior performance in the planetary spur gear test wherein a system of spur-type gears is driven under variable and very heavy loads. The lubricating fluid is circulated around the system by a pump and is maintained at between 95°C and 130°C. Samples of the lubricating fluid are removed periodically and analyzed for iron content. The test is terminated when excessive wear is recorded either by high iron levels in the oil, or by gear tooth breakage.

Still another feature of this invention is that the preferred additive combinations are capable of exhibiting superior (e.g., GL-5) performance properties even when blended with synthetic lubricants, a result which has seldom been achievable heretofore.

It will be understood and appreciated that unless otherwise specifically stated to the contrary, this invention is not intended to be limited, and indeed should not be limited, to products which pass specifically identified test procedures.

These and other features, advantages and embodiments of this invention will be still further apparent from the ensuing description and appended claims.

#### Mannich Base Dispersants.

As is well known, Mannich base dispersants are condensation products formed by condensing a long chain hydrocarbon-substituted phenol with one or more aliphatic aldehydes, usually formaldehyde or a formaldehyde precursor, and one or more polyamines, usually one or more polyalkylene polyamines. For use in the practice of this invention, the resultant Mannich base is boronated (sometimes called "borated") by reaction with a suitable boron compound such as a boron acid, a boron ester, a boron oxide, a salt of a boron acid, or the like.

Examples of Mannich condensation products, including in many cases boronated Mannich base dispersants, and methods for their production are described in the following U.S. Patents: 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277;

3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

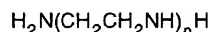
The polyamine group of the Mannich polyamine dispersants is derived from polyamine compounds characterized by containing a group of the structure -NH- wherein the two remaining valences of the nitrogen are satisfied by hydrogen, amino, or organic radicals bonded to said nitrogen atom. These compounds include aliphatic, aromatic, heterocyclic and carbocyclic polyamines. The source of the oil-soluble hydrocarbyl group in the Mannich polyamine dispersant is a hydrocarbyl-substituted hydroxy aromatic compound comprising the reaction product of a hydroxy aromatic compound, according to well known procedures, with a hydrocarbyl donating agent or hydrocarbon source. The hydrocarbyl substituent provides substantial oil solubility to the hydroxy aromatic compound and, preferably, is substantially aliphatic in character. Commonly, the hydrocarbyl substituent is derived from a polyolefin having at least about 40 carbon atoms. The hydrocarbon source should be substantially free from pendant groups which render the hydrocarbyl group oil insoluble. Examples of acceptable substituent groups are halide, hydroxy, ether, carboxy, ester, amide, nitro and cyano. However, these substituent groups preferably comprise no more than about 10 weight percent of the hydrocarbon source.

The preferred hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from suitable petroleum fractions or from olefin polymers, preferably polymers of mono-olefins having from 2 to about 30 carbon atoms. The hydrocarbon source can be derived, for example, from polymers of olefins such as ethylene, propene, 1-butene, isobutene, 1-octene, 1-methylcyclohexene, 2-butene and 3-pentene. Also useful are copolymers of such olefins with other polymerizable olefinic substances such as styrene. In general, these copolymers should contain at least 80 percent and preferably about 95 percent, on a weight basis, of units derived from the aliphatic mono-olefins to preserve oil solubility. The hydrocarbon source generally contains at least about 40 and preferably at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a number average molecular weight between about 600 and 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers.

The Mannich polyamine dispersants are generally prepared by reacting a hydrocarbyl-substituted hydroxy aromatic compound with an aldehyde and a polyamine. The aldehyde is typically an aliphatic aldehyde containing 1 to 7 carbon atoms, and in most cases is formaldehyde or a compound such as formalin or a polyformaldehyde from which formaldehyde is derived during the reaction. Typically, the substituted hydroxy aromatic compound is contacted with from about 0.1 to about 10 moles of polyamine and about 0.1 to about 10 moles of aldehyde per mole of substituted hydroxy aromatic compound. The reactants are mixed and heated to a temperature above about 80°C. to initiate the reaction. Preferably, the reaction is carried out at a temperature from about 100° to about 250°C. The resulting Mannich product has a predominantly benzylamine linkage between the aromatic compound and the polyamine. The reaction can be carried out in an inert diluent such as mineral oil, benzene, toluene, naphtha, ligroin, or other inert solvents to facilitate control of viscosity, temperature, and reaction rate.

Suitable polyamines for use in preparation of the Mannich polyamine dispersants include, but are not limited to, methylene polyamines, ethylene polyamines, propylene polyamines, butylene polyamines, pentylene polyamines, hexylene polyamines and heptylene polyamines. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also useful. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris (2-aminoethyl)amine, propylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, decamethylene diamine, di(heptamethylene) triamine, pentaethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2-aminopropyl)imidazoline, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs, obtained by condensing two or more of the above mentioned amines, are also useful, as are the polyoxyalkylene polyamines.

The most preferred amines are the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred. Methods for producing polyalkylene polyamines are known and reported in the literature. See for example U.S. Pat. Nos. 4,827,037; and 4,983,736; and EP Pub. Nos.

412,611; 412,612; 412,613; 412,614; and 412,615, and references cited therein.

The polyalkylene polyamines, examples of which are set forth above, are especially useful in preparing the Mannich polyamine dispersants for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of somewhat complex mixtures of polyalkylene polyamines which include cyclic condensation products such as piperazines. Because of their availability, these mixtures are particularly useful in preparing the Mannich polyamine dispersants. However, it will be appreciated that satisfactory dispersants can also be obtained by use of pure polyalkylene polyamines.

Alkylene diamines and polyalkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atom are also useful in preparing the Mannich polyamine dispersants. These materials are typically obtained by reaction of the corresponding polyamine with an epoxide such as ethylene oxide or propylene oxide. Preferred hydroxyalkyl-substituted diamines and polyamines are those in which the hydroxyalkyl groups have less than about 10 carbon atoms. Typical examples of suitable hydroxyalkyl-substituted diamines and polyamines include, but are not limited to, N-(2-hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxyethyl)ethylenediamine, mono(hydroxypropyl)diethylenetriamine, di(hydroxypropyl)tetraethylenepentamine and N-(4-hydroxybutyl)tetramethylenediamine. Higher homologs obtained by condensation of the above mentioned hydroxyalkyl-substituted diamines and polyamines through amine groups or through ether groups are also useful.

Amido-amine adducts such as are described in U.S. Pat. No. 5,034,018 can also be used in forming the Mannich base dispersants used in the practice of this invention.

Any conventional formaldehyde yielding reagent is useful for the preparation of the Mannich polyamine dispersants. Examples of such formaldehyde yielding reagents are trioxane, paraformaldehyde, trioxymethylene, aqueous formalin and gaseous formaldehyde. Other aldehydes which can be used include acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, hexanal, heptanal, and mixtures of two or more of these.

Typical procedures for producing boronated Mannich base ashless dispersants involve heating one or more such dispersants with at least one boron compound under conditions yielding a boron-containing composition. Suitable compounds of boron useful in forming boronated ashless dispersants suitable for use in the compositions of this invention include, for example, boron acids, boron oxides, boron esters, and amine or ammonium salts of boron acids. Illustrative compounds include boric acid (sometimes referred to as orthoboric acid), boronic acid, tetraboric acid, metaboric acid, pyroboric acid, esters of such acids, such as mono-, di-, and tri-organic esters with alcohols or polyols having up to 20 or more carbon atoms (e.g., methanol, ethanol, 2-propanol, propanol, butanols, pentanols, hexanols, ethylene glycol, propylene glycol, trimethylol propane, diethanol amine, etc.), boron oxides such as boric oxide and boron oxide hydrate, and ammonium salts such as ammonium borate, ammonium pyroborate, etc. While usable, boron halides such as boron trifluoride, boron trichloride, and the like, are undesirable as they tend to introduce halogen atoms into the boronated dispersant, a feature which is detrimental from the environmental, toxicological and conservation standpoints. Amine borane addition compounds and hydrocarbyl boranes can also be used, although they tend to be relatively expensive. The preferred boron reagent is boric acid,  $H_3BO_3$ .

The most preferred Mannich base dispersants for use in this invention are boronated Mannich base ashless dispersants formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to 2.5 moles of formaldehyde and from about 0.5 to 2 moles of polyalkylene polyamine, and by boronating the resultant condensation product.

#### Sulphur-Containing Antiwear and/or Extreme Pressure Agents.

A variety of oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure additives can be used in the practice of this invention. Examples are included within the categories of dihydrocarbyl polysulphides; sulphurized olefins; sulphurized fatty acid esters of both natural and synthetic origins; trithiones; sulphurized thienyl derivatives; sulphurized terpenes; sulphurized oligomers of  $C_2$ - $C_8$  monoolefins; and sulphurized Diels-Alder adducts. Such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulphurized polyisobutene of Mn 1,100, sulphurized isobutylene, sulphurized diisobutylene, sulphurized triisobutylene, dicyclohexyl polysulphide, diphenyl polysulphide, dibenzyl polysulphide, dinonyl polysulphide, and mixtures of di-tert-butyl polysulphide such as mixtures of di-tert-butyl trisulphide, di-tert-butyl tetrasulphide and di-tert-butyl pentasulphide, among others. Combinations of such categories of sulphur-containing antiwear and/or extreme pressure agents can also be used, such as a combination of sulphurized isobutylene and di-tert-butyl trisulphide, a combination of sulphurized isobutylene and dinonyl trisulphide, a combination of sulphurized tall oil and dibenzyl polysulphide, and the like.

One type of sulphur-containing antiwear and/or extreme pressure agents is comprised of the oil-soluble active sulphur-containing antiwear and/or extreme pressure agents. Generally speaking, these are substances which possess a linkage of two or more sulphur atoms (e.g., -S-S-, -S-S-S-, -S-S-S-S-, S-S-S-S-S-, etc.).

To determine whether a sulphur-containing material is an active sulphur-containing material, use is made of a copper coupon corrosion test conducted as follows: A copper coupon approximately 70 x 15 mm and about 1.25 mm in thickness is cleaned by use of steel wool (0000 grade), washed with heptane, and then with acetone, dried, and weighed to the nearest 0.1 mg. The cleaned coupon is placed in a test tube and covered completely with the composition to be tested, and the system is heated to 125°C by means of an oil bath. After holding the system at 125°C for three hours, the copper coupon is removed from the test tube, rinsed with heptane, and then with acetone. The dried coupon is then rubbed with a paper towel moistened with acetone to remove any surface flakes formed by copper corrosion. The coupon is then air-dried and weighed to the nearest 0.1 mg. The difference in weight between the initial copper coupon and the coupon after the test represents the extent to which the copper was corroded under the test conditions. Therefore the larger the weight difference, the greater the copper corrosion, and thus the more active the sulphur compound. If the coupon weight loss is 30 milligrams or more, the sulphur-containing agent is considered "active".

Another type of sulphur-containing antiwear and/or extreme pressure agents suitable for use in the practice of this invention is comprised of "non-active" sulphur-containing additives. These are materials which when subjected to the above copper coupon corrosion test give a weight loss of less than 30 milligrams. Examples of materials falling in this category include Anglamol 33 additive (a sulphurized isobutylene product of The Lubrizol Corporation), distilled di-tert-butyl trisulphide, and the like.

Because of the toxicity of hydrogen sulphide, it is preferable, though not essential, to utilize in the practice of this invention oil-soluble sulphur-containing antiwear and/or extreme pressure agents, and more preferably oil-soluble active sulphur-containing antiwear and/or extreme pressure agents, that yield less than 25 ppm, and more preferably less than 10 ppm, of vapor space H<sub>2</sub>S when heated in the concentrated state for one week at 65°C. Most preferred are materials of this type which yield no detectable vapor space H<sub>2</sub>S when tested under these conditions.

The most preferred oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agents from the cost-effectiveness standpoint are the sulphurized olefins containing at least 30% by weight of sulphur, the dihydrocarbyl polysulphides containing at least 25% by weight of sulphur, and mixtures of such sulphurized olefins and polysulphides. Of these materials, sulphurized isobutylene having a sulphur content of at least 40% by weight and a chlorine content of less than 0.2% by weight is the most especially preferred material.

Methods of preparing sulphurized olefins are described in U.S. Pat. Nos. 2,995,569; 3,673,090; 3,703,504; 3,703,505; 3,796,661; and 3,873,454. Also useful are the sulphurized olefin derivatives described in U.S. Pat. No. 4,654,156.

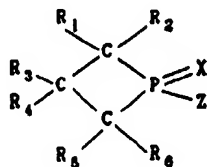
#### Phosphorus-Containing Antiwear and/or Extreme Pressure Agents.

For purposes of this invention a component which contains both phosphorus and sulphur in its chemical structure is deemed a phosphorus-containing antiwear and/or extreme pressure agent rather than a sulphur-containing antiwear and/or extreme pressure agent.

Although use can be made of a wide variety of oil-soluble substances such as the oil-soluble organic phosphates, organic phosphites, organic phosphonates, organic phosphonites, etc., and their sulphur analogs, the preferred phosphorus-containing antiwear and/or extreme pressure agents for use in the compositions of this invention are those which contain both phosphorus and nitrogen.

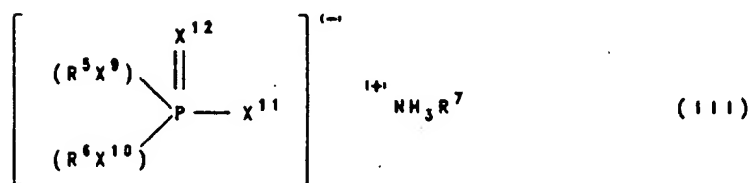
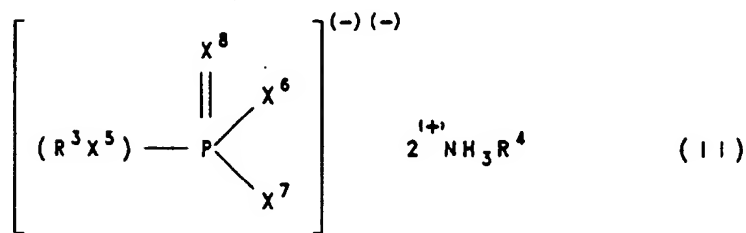
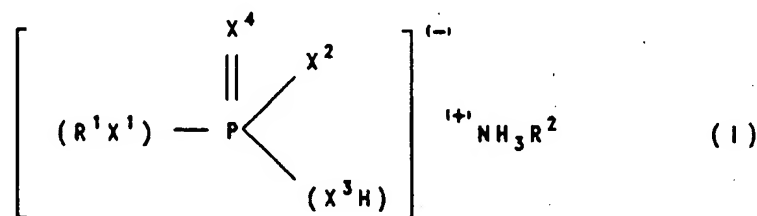
One such type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additives which can be employed in the practice of this invention are the phosphorus- and nitrogen-containing compositions of the type described in G.B. 1,009,913; G.B. 1,009,914; U.S. 3,197,405 and/or U.S. 3,197,496. In general, these compositions are formed by forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine or hydroxy-substituted amine.

Another type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additive which can be used in the compositions of this invention is the amine salts of hydroxy-substituted phosphetanes or the amine salts of hydroxy-substituted thiophosphetanes. Typically, such salts are derived from compounds of the formula



wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  is a hydrogen atom or a carbon-bonded organic group such as a hydrocarbyl group or a substituted hydrocarbyl group wherein the substituent(s) do(es) not materially detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group; X is a sulphur or an oxygen atom and Z is a hydroxyl group or an organic group having one or more acidic hydroxyl groups. Examples of this general type of antiwear and/or extreme pressure agent include the amine salts hydroxyphosphetanes and the amine salts of hydroxy-thiophosphetanes typified by Irgalube 295 additive (Ciba-Geigy Corporation).

Another useful category of phosphorus- and nitrogen-containing antiwear and/or extreme pressure agents is comprised of the amine salts of partial esters of phosphoric and thiophosphoric acids. Such compounds may be collectively represented by the formulas I, II, and III as follows:



or mixtures thereof. In Formulas I, II and III, each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ , and  $R^7$  is, independently, a hydrocarbyl group and each of  $X^1$ ,  $X^2$ ,  $X^3$ ,  $X^4$ ,  $X^5$ ,  $X^6$ ,  $X^7$ ,  $X^8$ ,  $X^9$ ,  $X^{10}$ ,  $X^{11}$ , and  $X^{12}$  is, independently, an oxygen atom or a sulphur atom.

In one preferred sub-category the amine salts are formed with one or more partially esterified monothiophosphoric acids. These are compounds of Formulas (I), (II), and (III) above wherein only one of  $X^1$ ,  $X^2$ ,  $X^3$ , and  $X^4$ , only one of  $X^5$ ,  $X^6$ ,  $X^7$ , and  $X^8$ , and only one of  $X^9$ ,  $X^{10}$ ,  $X^{11}$ , and  $X^{12}$  is a sulphur atom.

In another preferred sub-category the amine salts are formed with one or more partially esterified phosphoric acids. These are compounds of Formulas (I), (II), and (III) above wherein all of  $X^1$ ,  $X^2$ ,  $X^3$ ,  $X^4$ ,  $X^5$ ,  $X^6$ ,  $X^7$ ,  $X^8$ ,  $X^9$ ,  $X^{10}$ ,  $X^{11}$ , and  $X^{12}$  are oxygen atoms.

Another preferred sub-category of amine salts are those formed with one or more partially esterified dithiophos-



phoric acids. These are compounds of Formulas (I), (II), and (III) above wherein two of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup>, and X<sup>4</sup>, two of X<sup>5</sup>, X<sup>6</sup>, X<sup>7</sup>, and X<sup>8</sup>, and two of X<sup>9</sup>, X<sup>10</sup>, X<sup>11</sup>, and X<sup>12</sup> are sulphur atoms.

Also useful are amine salts of Formulas (I), (II), and (III) above wherein three or four of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup>, and X<sup>4</sup>, three or four of X<sup>5</sup>, X<sup>6</sup>, X<sup>7</sup>, and X<sup>8</sup>, and three or four of X<sup>9</sup>, X<sup>10</sup>, X<sup>11</sup>, and X<sup>12</sup> are sulphur atoms.

While all of the above oil-soluble amine salts are useful as components in the compositions of this invention, it is most preferred to include at least one oil-soluble amine salt of a dihydrocarbyl monothiophosphoric acid (one sulphur atom per molecule), either alone or in combination with at least one oil-soluble amine salt of a dihydrocarbyl phosphoric acid (no sulphur atom in the molecule).

Suitable salts or amine adducts of the partially esterified monothiophosphoric acids include such compounds as:

Octylamine salt of O-monobutylthiophosphoric acid  
 Octylamine salt of S-monobutylthiophosphoric acid  
 Octylamine salt of O-monobutylthionophosphoric acid  
 Octylamine salt of O,O-dibutylthiophosphoric acid  
 Octylamine salt of O,S-dibutylthiophosphoric acid  
 Octylamine salt of O,O-dibutylthionophosphoric acid  
 Octylamine salt of O-monoisobutylthiophosphoric acid  
 Octylamine salt of S-monoisobutylthiophosphoric acid  
 Octylamine salt of O-monoisobutylthionophosphoric acid  
 Octylamine salt of O,O-diisobutylthiophosphoric acid  
 Octylamine salt of O,S-diisobutylthiophosphoric acid  
 Octylamine salt of O,O-diisobutylthionophosphoric acid  
 Octylamine salt of O-monoamylthiophosphoric acid  
 Octylamine salt of S-monoamylthiophosphoric acid  
 Octylamine salt of O-monoamylthionophosphoric acid  
 Octylamine salt of O,O-diamylthiophosphoric acid  
 Octylamine salt of O,S-diamylthiophosphoric acid  
 Octylamine salt of O,O-diamylthionophosphoric acid  
 Octylamine salt of O-monoheptylthiophosphoric acid  
 Octylamine salt of S-monoheptylthiophosphoric acid  
 Octylamine salt of O-monoheptylthionophosphoric acid  
 Octylamine salt of O,O-diheptylthiophosphoric acid  
 Octylamine salt of O,S-diheptylthiophosphoric acid  
 Octylamine salt of O,O-diheptylthionophosphoric acid  
 Octylamine salt of O-monoheptylthiophosphoric acid  
 Octylamine salt of S-monoheptylthiophosphoric acid  
 Octylamine salt of O-monoheptylthionophosphoric acid  
 Octylamine salt of O,O-diheptylthiophosphoric acid  
 Octylamine salt of O,S-diheptylthiophosphoric acid  
 Octylamine salt of O,O-diheptylthionophosphoric acid  
 Octylamine salt of O-mono-2-ethylhexylthiophosphoric acid  
 Octylamine salt of S-mono-2-ethylhexylthiophosphoric acid  
 Octylamine salt of O-mono-2-ethylhexylthionophosphoric acid  
 Octylamine salt of O,O-di-2-ethylhexylthiophosphoric acid  
 Octylamine salt of O,S-di-2-ethylhexylthiophosphoric acid  
 Octylamine salt of O,O-di-2-ethylhexylthionophosphoric acid  
 Octylamine salt of O-mono-octylthiophosphoric acid  
 Octylamine salt of S-mono-octylthiophosphoric acid  
 Octylamine salt of O-mono-octylthionophosphoric acid  
 Octylamine salt of O,O-dioctylthiophosphoric acid  
 Octylamine salt of O,S-dioctylthiophosphoric acid  
 Octylamine salt of O,O-dioctylthionophosphoric acid  
 Octylamine salt of O-monononylthiophosphoric acid  
 Octylamine salt of S-monononylthiophosphoric acid  
 Octylamine salt of O-mono-nonylthionophosphoric acid  
 Octylamine salt of O,O-dinonylthiophosphoric acid  
 Octylamine salt of O,S-dinonylthiophosphoric acid  
 Octylamine salt of O,O-dinonylthionophosphoric acid

Octylamine salt of O-monodecylthiophosphoric acid  
 Octylamine salt of S-monodecylthiophosphoric acid  
 Octylamine salt of O-monodecylthionophosphoric acid  
 Octylamine salt of O,O-didecylthiophosphoric acid  
 5 Octylamine salt of O,S-didecylthiophosphoric acid  
 Octylamine salt of O,O-didecylthionophosphoric acid  
 Octylamine salt of O-monododecylthiophosphoric acid  
 Octylamine salt of S-monododecylthiophosphoric acid  
 Octylamine salt of O-monododecylthionophosphoric acid  
 10 Octylamine salt of O,O-didodecylthiophosphoric acid  
 Octylamine salt of O,S-didodecylthiophosphoric acid  
 Octylamine salt of O,O-didodecylthionophosphoric acid  
 Octylamine salt of O-monotridecylthiophosphoric acid  
 Octylamine salt of S-monotridecylthiophosphoric acid  
 15 Octylamine salt of O-monotridecylthionophosphoric acid  
 Octylamine salt of O,O-ditridecylthiophosphoric acid  
 Octylamine salt of O,S-ditridecylthiophosphoric acid  
 Octylamine salt of O,O-ditridecylthionophosphoric acid  
 Octylamine salt of O-monotetradecylthiophosphoric acid  
 20 Octylamine salt of S-monotetradecylthiophosphoric acid  
 Octylamine salt of O-monotetradecylthionophosphoric acid  
 Octylamine salt of O,O-ditetradecylthiophosphoric acid  
 Octylamine salt of O,S-ditetradecylthiophosphoric acid  
 Octylamine salt of O,O-ditetradecylthionophosphoric acid  
 25 Octylamine salt of O-monohexadecylthiophosphoric acid  
 Octylamine salt of S-monohexadecylthiophosphoric acid  
 Octylamine salt of O-monohexadecylthionophosphoric acid  
 Octylamine salt of O,O-dihexadecylthiophosphoric acid  
 Octylamine salt of O,S-dihexadecylthiophosphoric acid  
 30 Octylamine salt of O,O-dihexadecylthionophosphoric acid  
 Octylamine salt of O-monooctadecylthiophosphoric acid  
 Octylamine salt of S-monooctadecylthiophosphoric acid  
 Octylamine salt of O-monooctadecylthionophosphoric acid  
 Octylamine salt of O,O-diocetadecylthiophosphoric acid  
 35 Octylamine salt of O,S-diocetadecylthiophosphoric acid  
 Octylamine salt of O,O-diocetadecylthionophosphoric acid  
 Octylamine salt of O-monooleythiophosphoric acid  
 Octylamine salt of S-monooleythiophosphoric acid  
 Octylamine salt of O-monooleythionophosphoric acid  
 40 Octylamine salt of O,O-dioleythiophosphoric acid  
 Octylamine salt of O,S-dioleythiophosphoric acid  
 Octylamine salt of O,O-dioleythionophosphoric acid  
 Octylamine salt of O-monobenzylthiophosphoric acid  
 Octylamine salt of S-monobenzylthiophosphoric acid  
 45 Octylamine salt of O-monobenzylthionophosphoric acid  
 Octylamine salt of O,O-dibenzylthiophosphoric acid  
 Octylamine salt of O,S-dibenzylthiophosphoric acid  
 Octylamine salt of O,O-dibenzylthionophosphoric acid  
 Octylamine salt of O-monocyclohexylthiophosphoric acid  
 50 Octylamine salt of S-monocyclohexylthiophosphoric acid  
 Octylamine salt of O-monocyclohexylthionophosphoric acid  
 Octylamine salt of O,O-dicyclohexylthiophosphoric acid  
 Octylamine salt of O,S-dicyclohexylthiophosphoric acid  
 Octylamine salt of O,O-dicyclohexylthionophosphoric acid  
 55 Octylamine salt of O-mono-p-tolylthiophosphoric acid  
 Octylamine salt of S-mono-p-tolylthiophosphoric acid  
 Octylamine salt of O-mono-p-tolylthionophosphoric acid  
 Octylamine salt of O,O-di-p-tolylthiophosphoric acid

Octylamine salt of O,S-di-p-tolylthiophosphoric acid  
 Octylamine salt of O,O-di-p-tolylthionophosphoric acid  
 Octylamine salt of O-monoxylylthiophosphoric acid  
 Octylamine salt of S-monoxylylthiophosphoric acid  
 5 Octylamine salt of O-monoxylylthionophosphoric acid  
 Octylamine salt of O,O-dixylylthiophosphoric acid  
 Octylamine salt of O,S-dixylylthiophosphoric acid  
 Octylamine salt of O,O-dixylylthionophosphoric acid  
 Octylamine salt of O-isopropyl-O-octadecylthiophosphoric acid  
 10 Octylamine salt of O-nonyl-S-butylthiophosphoric acid  
 Octylamine salt of O-undecyl-O-methylthionophosphoric acid  
 Octylamine salt of O-cyclohexyl-S-decylthiophosphoric acid  
 Octylamine salt of O-phenyl-S-tetradecylthiophosphoric acid  
 Octylamine salt of O-pentadecyl-O-cyclohexenylthionophosphoric acid  
 15 Octylamine salt of O-ethyl-O-(p-tert-amyphenyl)thionophosphoric acid  
 Octylamine salt of O-benzyl-S-isononylthiophosphoric acid  
 Octylamine salt of O-cyclopentyl-O-heptadecylthionophosphoric acid  
 Octylamine salt of O-oley-S-butylthiophosphoric acid  
 Octylamine salt of O-2-ethylhexyl-O-isooctylthionophosphoric acid  
 20 Octylamine salt of O-allyl-S-tridecylthiophosphoric acid.

It will be noted that in the above listing of illustrative amine salts, the partially esterified monothiophosphoric acids have been named, for convenience, by use of the "thio-thiono" system of nomenclature in which thiono refers to a sulphur atom bonded to the phosphorus atom by a double bond whereas thio refers to a sulphur atom that is bonded to the phosphorus atom by a single bond. Such compounds can also be named by use of a "thioic" system of nomenclature. For example, O,O-dihydrocarbylthionophosphoric acid is also known as O,O-dihydrocarbylphosphorothioic acid,  $(RO)_2P(S)(OH)$ . However, except when referring to specific compounds (as in the above "thio-thiono" listing) the term "monothiophosphoric acid" is used generically herein to refer to phosphoric acid having only one sulphur atom, and that sulphur atom can be bonded to the phosphorus atom either by a single bond or by a double bond. Likewise except when referring to specific compounds, the term "dithiophosphoric acid" refers to phosphoric acid having two sulphur atoms both of which can be bonded to the phosphorus atom by single bonds, or one of which is bonded to the phosphorus atom by a double bond and the other of which is bonded to the phosphorus atom by single bond. The same applies to the term "trithiophosphoric acid", wherein two of the three sulphur atoms can be bonded to the phosphorus atom by single bonds and the third by either a single or double bond.

Illustrative examples of amine salts of partial esters of phosphoric acid include the following:

Octylamine salt of monobutylphosphoric acid  
 Octylamine salt of dibutylphosphoric acid  
 Octylamine salt of monoisobutylphosphoric acid  
 40 Octylamine salt of diisobutylphosphoric acid  
 Octylamine salt of monoamylphosphoric acid  
 Octylamine salt of diamylphosphoric acid  
 Octylamine salt of monohexylphosphoric acid  
 Octylamine salt of dihexylphosphoric acid  
 45 Octylamine salt of monoheptylphosphoric acid  
 Octylamine salt of diheptylphosphoric acid  
 Octylamine salt of mono-2-ethylhexylphosphoric acid  
 Octylamine salt of di-2-ethylhexylphosphoric acid  
 Octylamine salt of monooctylphosphoric acid  
 50 Octylamine salt of dioctylphosphoric acid  
 Octylamine salt of monononylphosphoric acid  
 Octylamine salt of dinonylphosphoric acid  
 Octylamine salt of monodecylphosphoric acid  
 Octylamine salt of didecylphosphoric acid  
 55 Octylamine salt of monododecylphosphoric acid  
 Octylamine salt of didodecylphosphoric acid  
 Octylamine salt of monotridecylphosphoric acid  
 Octylamine salt of ditridecylphosphoric acid

Octylamine salt of monotetradecylphosphoric acid  
 Octylamine salt of ditetradecylphosphoric acid  
 Octylamine salt of monohexadecylphosphoric acid  
 Octylamine salt of dihexadecylphosphoric acid  
 5 Octylamine salt of monooctadecylphosphoric acid  
 Octylamine salt of dioctadecylphosphoric acid  
 Octylamine salt of monooleylphosphoric acid  
 Octylamine salt of diolelylphosphoric acid  
 Octylamine salt of monobenzylphosphoric acid  
 10 Octylamine salt of dibenzylphosphoric acid  
 Octylamine salt of monocyclohexylphosphoric acid  
 Octylamine salt of dicyclohexylphosphoric acid  
 Octylamine salt of mono-p-tolylphosphoric acid  
 Octylamine salt of di-p-tolylphosphoric acid  
 15 Octylamine salt of monoxilylphosphoric acid  
 Octylamine salt of dixilylphosphoric acid  
 Octylamine salt of monoisopropyl-monooctadecylphosphoric acid  
 Octylamine salt of monononyl-monobutylphosphoric acid  
 Octylamine salt of monoundecyl-monomethylphosphoric acid  
 20 Octylamine salt of monocyclohexyl-monodecylphosphoric acid  
 Octylamine salt of monophenyl-monotetradecylphosphoric acid  
 Octylamine salt of monopentadecyl-monocyclohexenylphosphoric acid  
 Octylamine salt of monoethyl-mono(p-tert-amyphenyl)phosphoric acid  
 Octylamine salt of monobenzyl-monoisononylphosphoric acid  
 25 Octylamine salt of monocyclopentyl-monoheptadecylphosphoric acid  
 Octylamine salt of monooleyl-monobutylphosphoric acid  
 Octylamine salt of mono-(2-ethylhexyl)-monoisooctylphosphoric acid  
 Octylamine salt of monoallyl-monotridecylphosphoric acid.

30 Examples of corresponding amine salts of partially esterified dithiophosphoric acid, of partially esterified trithiophosphoric acid, and of partially esterified tetrathiophosphoric acid will be readily apparent from the above listings.

Octylamine salts or adducts have been set forth in the above two listings merely for purposes of illustration. In lieu of octyl amine salts, or in addition thereto, use can be made of nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, cyclohexylamine, phenylamine, mesitylamine, oleylamine, cocoamine, soyamine, C<sub>8</sub> tertiary alkyl primary amine, C<sub>12-14</sub> tertiary alkyl primary amine, C<sub>22-24</sub> tertiary alkyl primary amine, phenethylamine, etc., salts or adducts of partially esterified phosphoric, monothiophosphoric, dithiophosphoric, trithiophosphoric, and/or tetrathiophosphoric acids, including mixtures of any such compounds. Generally speaking, the preferred amine salts are salts of aliphatic amines, especially the saturated or olefinically unsaturated aliphatic primary amines, such as n-octylamine, 2-ethylhexylamine, tert-octylamine, n-decylamine, the C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub> and C<sub>16</sub> tertiary alkyl primary amines (either singly or in any combinations thereof, such as a mixture of the C<sub>12</sub> and C<sub>14</sub> tertiary alkyl primary amines), n-undecylamine, a mixture of C<sub>14</sub> to C<sub>18</sub> tertiary alkyl primary amines, laurylamine, hexadecylamine, heptadecylamine, octadecylamine, the C<sub>22</sub> and C<sub>24</sub> tertiary alkyl primary amines (either singly or in combination), decenylamine, dodecenylamine, palmitoleylamine, oleylamine, linoleylamine, eicosenylamine, etc. Secondary hydrocarbyl amines and tertiary hydrocarbyl amines can also be used either alone or in combination with each other or in combination with primary amines. Thus any combination of primary, secondary and/or tertiary amines, whether monoamine or polyamine, can be used in forming the salts or adducts.

45 Similarly, the amines used can be in the form of polyalkylene polyamines; functionally-substituted polyamines such as a succinimide or succinamide of a polyalkylene polyamines such as a polyisobutenyl succinimide of diethylene triamine, a polyisobutenyl succinimide of triethylene tetramine, a polyisobutenyl succinimide of tetraethylene pentamine, a polyisobutenyl succinimide of pentaethylene hexamine (including succinimides made from commercially available polyethylene polyamine mixtures which contain linear, branched and cyclic species); and Mannich bases derived from polyalkylene polyamines of the types just described. Moreover, the polyalkylene polyamines whether in the free state or in the form of a succinimide, succinamide, or Mannich base, can be partially boronated, partially phosphorylated, or partially acylated with a reagent such as maleic anhydride, malic acid, itaconic acid, itaconic anhydride, thiomalic acid, fumaric acid, and the like, provided that such boronated or phosphorylated or acylated amine or amine moiety contains at least sufficient residual basicity to enable it to form a salt with the partially esterified phosphoric or thiophosphoric acid. Alkylene polyamines in the form of succinimides, succinamides or Mannich bases which have been boronated and phosphorylated are described for example in U.S. Pat. No. 4,857,214.

Use of primary amines is preferred. Especially preferred amines are alkyl monoamines and alkenyl monoamines having from about 8 to about 24 carbon atoms in the molecule.

Amines having less than 8 carbon atoms can be used, including methyl amine, etc., provided the resultant amine salt is oil-soluble. Likewise, amines having more than 24 carbon atoms can be used, again with the proviso that the resultant amine salt is oil soluble.

Methods for the preparation of such amine salts are well known and reported in the literature. See for example, U.S. Pat. Nos. 2,063,629; 2,224,695; 2,447,288; 2,616,905; 3,984,448; 4,431,552; Pesin et al, *Zhurnal Obshchei Khimii*, Vol. 31, No. 8, pp. 2508-2515 (1961); and International Application Publication No. WO 87/07638.

It should be noted that amine salts of partially esterified monothiophosphoric acids are usually made by reacting a mono- and/or dihydrocarbyl phosphite with sulphur or an active sulphur-containing compound such as are referred to above under the caption "Sulphur-Containing Antiwear and/or Extreme Pressure Agents" and one or more primary or secondary amines. Such reactions tend to be highly exothermic reactions which can become uncontrollable, if not conducted properly. One preferred method of forming these amine salts involves a process which comprises (i) introducing, at a rate such that the temperature does not exceed about 60°C, one or more dihydrocarbyl hydrogen phosphites, such as a dialkyl hydrogen phosphite, into an excess quantity of one or more active sulphur-containing materials, such as sulphurized branched-chain olefin (e.g., isobutylene, diisobutylene, triisobutylene, etc.), while agitating the mixture so formed, (ii) introducing into this mixture, at a rate such that the temperature does not exceed about 60°C, one or more aliphatic primary or secondary amines, preferably one or more aliphatic primary monoamines having in the range of about 8 to about 24 carbon atoms per molecule while agitating the mixture so formed, and (iii) maintaining the temperature of the resultant agitated reaction mixture at between about 55 and about 60°C until reaction is substantially complete. Another suitable way of producing these amine salts is to concurrently introduce all three of the reactants into the reaction zone at suitable rates and under temperature control such that the temperature does not exceed about 60°C. Another preferred way of forming amine salts of partially esterified monothiophosphoric acids is to pre-react elemental sulphur with the amine for a short period of time and then add thereto the appropriate dihydrocarbyl hydrogen phosphite at a rate such that the temperature does not become excessive and the reaction uncontrollable.

#### Amine Salts of Carboxylic Acids.

Another component for use in the compositions of this invention is one or more amine salts of one or more long chain carboxylic acids. The acids can be monocarboxylic acids or polycarboxylic acids. Generally speaking, these acids contain from about 8 to about 50 carbon atoms in the molecule and thus the salts are oil-soluble. A variety of amines can be used in forming such salts, including primary, secondary and tertiary amines, and the amines can be monoamines, or polyamines. Further, the amines may be cyclic or acyclic aliphatic amines, aromatic amines, heterocyclic amines, or amines containing various mixtures of acyclic and cyclic groups.

Preferred amine salts include the alkyl and alkenyl amine salts of alkanolic acids and/or alkenolic acids, the alkyl and alkenyl amine salts of alkanedioic acids and/or alkenedioic acids and any combination of the foregoing.

The amine salts are formed by classical chemical reactions, namely, the reaction of an amine or mixture of amines, with the appropriate acid or mixture of acids. Accordingly, further discussion concerning methods for the preparation of such materials would be redundant.

Among the amine salts of long-chain acids that may be used are the following: the octyl amine salt of C<sub>36</sub> dimer acid (made by dimerization of linoleic acid), lauryl ammonium laurate (i.e. the lauryl amine salt of lauric acid), stearyl ammonium laurate, cyclohexyl ammonium laurate, octyl ammonium laurate, pyridine laurate, aniline laurate, lauryl ammonium stearate, stearyl ammonium stearate, cyclohexyl ammonium stearate, octyl ammonium stearate, pyridine stearate, aniline stearate, lauryl ammonium octanoate, stearyl ammonium octanoate, cyclohexyl ammonium octanoate, octyl ammonium octanoate, pyridine octanoate, aniline octanoate, nonyl ammonium laurate, nonyl ammonium stearate, nonyl ammonium octanoate, lauryl ammonium nonanoate, stearyl ammonium nonanoate, cyclohexyl ammonium nonanoate, octyl ammonium nonanoate, pyridine nonanoate, aniline nonanoate, nonyl ammonium nonanoate, lauryl ammonium decanoate, stearyl ammonium decanoate, cyclohexyl ammonium decanoate, octyl ammonium decanoate, pyridine decanoate, aniline decanoate, decyl ammonium laurate, decyl ammonium stearate, decyl ammonium octanoate, decyl ammonium nonanoate, decyl ammonium decanoate, bis octyl amine salt of suberic acid, bis cyclohexyl amine salt of suberic acid, bis lauryl amine salt of suberic acid, bis stearyl amine salt of suberic acid, bis octyl amine salt of sebacic acid, bis cyclohexyl amine salt of sebacic acid, bis lauryl amine salt of sebacic acid, bis stearyl amine salt of sebacic acid, the tert-dodecyl and tert-tetradecyl primary amine salts of octanoic acid, the tert-decyl and tert-dodecyl primary amine salts of octanoic acid, the tert-dodecyl and tert-tetradecyl primary amine salts of lauric acid, the tert-decyl and tert-dodecyl primary amine salts of lauric acid, the tert-dodecyl and tert-tetradecyl primary amine salts of stearic acid, the tert-decyl and tert-dodecyl primary amine salts of stearic acid, the hexyl amine salt of C<sub>24</sub>-dicarboxylic acid, the octyl amine salt of C<sub>28</sub>-dicarboxylic acid, the octyl amine salt of C<sub>30</sub>-dicarboxylic acid, the decyl

amine salt of C<sub>30</sub>-dicarboxylic acid, the octyl amine salt of C<sub>32</sub>-dicarboxylic acid, the bis lauryldimethyl amine salt of traumatic acid, diethyl ammonium laurate, dioctyl ammonium laurate, dicyclohexyl ammonium laurate, diethyl ammonium octanoate, dioctyl ammonium octanoate, dicyclohexyl ammonium octanoate, diethyl ammonium stearate, dioctyl ammonium stearate, diethyl ammonium stearate, dibutyl ammonium stearate, dicyclopentyl ammonium stearate, dipropyl ammonium benzoate, didecyl ammonium benzoate, dimethylcyclohexyl ammonium benzoate, triethyl ammonium laurate, triethyl ammonium octanoate, triethyl ammonium stearate, triethyl ammonium benzoate, trioctyl ammonium laurate, trioctyl ammonium octanoate, trioctyl ammonium stearate, trioctyl ammonium benzoate, and the like. It will be understood of course that the amine salt of the monocarboxylic and/or polycarboxylic acid used should be sufficiently soluble in the base oil used as to provide homogeneous solution at the concentration employed.

Among the preferred amine salts for use in practice of this invention are the primary amine salts of long chain monocarboxylic acids in which the amine thereof is a monoalkyl monoamine, RNH<sub>2</sub>; the secondary amine salts of long chain monocarboxylic acids in which the amine thereof is a dialkyl monoamine, R<sub>2</sub>NH; the tertiary amine salts of long chain monocarboxylic acids in which the amine thereof is a trialkyl monoamine, R<sub>3</sub>N; the bis primary amine salts of long chain dicarboxylic acids in which the amine thereof is a monoalkyl monoamine, RNH<sub>2</sub>; the bis secondary amine salts of long chain dicarboxylic acids in which the amine thereof is a dialkyl monoamine, R<sub>2</sub>NH; the bis tertiary amine salts of long chain dicarboxylic acids in which the amine thereof is a trialkyl monoamine, R<sub>3</sub>N; and mixtures thereof. In the foregoing formulae, R is an alkyl group which contains up to about 30 or more carbon atoms, and preferably from about 6 to about 24 carbon atoms.

#### Amines.

The free amines which can be used in forming the compositions of this invention can be any of the amines referred to above in connection with the amine salts of partial esters of phosphoric acid or thiophosphoric acids or in connection with the amine salts of carboxylic acids, provided that the amines are oil-soluble. Of the various amines, the preferred type is composed of alkyl primary monoamines, and alkenyl primary monoamines, especially those containing from about 6 to about 24 carbon atoms. Examples of such amines include hexylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, eicosylamine, docosylamine, tetracosylamine, oleylamine, cocoamine, soyamine, C<sub>12-14</sub> tertiary alkyl primary amine, C<sub>22-24</sub> tertiary alkyl primary amine, and the like.

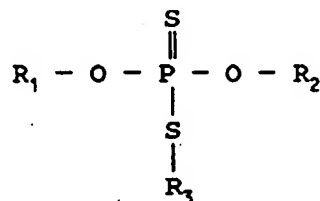
Generally speaking, the free amine used in the compositions will correspond to the amine used in forming either the amine salt of the phosphorus acid or the amine salt of the carboxylic acid, or both.

It will be understood and appreciated that the term "free amine" refers to the form of the amine as it is charged into the blender or mixing vessel in which the additive concentrate or the lubricating oil or functional fluid composition is being formed. Some or all of the free amine may complex with or react with other components being used in the product being formed, such as acidic additive components. Thus the term "free amine" does not signify or imply that the amine must remain free -- all or part of it may remain uncomplexed and unreacted, but this is not a requirement.

It will also be understood and appreciated that components such as amine salts of phosphorus acids and amine salts of carboxylic acid can be preformed prior to being formulated in a composition of this invention, or such components can, in whole or in part, be formed in situ.

#### Trihydrocarbyl Esters of Dithiophosphoric Acids.

This group of compounds is composed of O,O-dihydrocarbyl-S-hydrocarbyl thiothionophosphates (also known as O,O-dihydrocarbyl-S-hydrocarbyl phosphorothiothionates) which can be represented by the general formula:



wherein each of R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> is independently a hydrocarbyl group, especially where R<sub>3</sub> is an alicyclic hydrocarbyl group. Particularly preferred are the O,O-dialkyl-S-hydrocarbyl phosphorothiothionates wherein R<sub>3</sub> is an alicyclic group and R<sub>1</sub> and R<sub>2</sub> are alkyl groups each having up to about 18 carbon atoms and most preferably up to about 12 carbon

atoms.

These compounds can be made by various known methods. Probably the most efficacious method involves reacting phosphorus pentasulphide ( $P_2S_5$ , often regarded as  $P_4S_{10}$ ) with the appropriate alcohols or mixture of alcohols. Compounds in which one of the hydrocarbonyl groups differs from the other two are preferably made by first reacting the phosphorus pentasulphide with an appropriate alcohol to form an intermediate product, viz.  $(RO)_2PSSH$ , which in turn is reacted with a compound containing at least one reactive olefinic double bond. Note, for example, U.S. Pat. Nos. 2,528,732, 2,561,773, 2,665,295, 2,767,206, 2,802,856, 3,023,209, and *J. Org. Chem.*, 1963, 28, 1262-8.

Exemplary compounds suitable for use in the compositions of this invention include such compounds as trioctylphosphorothiothionate, tridecylphosphorothiothionate, triaurylphosphorothiothionate, O,O-diethyl bicyclo[2.2.1]-hepten-2-yl phosphorothiothionate, O,O-diethyl 7,7-dimethyl-bicyclo[2.2.1]-5-hepten-2-yl phosphorothiothionate, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with cis-endomethylene-tetrahydrophthalic acid dimethyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with cis-endomethylene-tetrahydrophthalic acid dibutyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with cis-endomethylene-tetrahydrophthalic acid dilauryl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-1-methyl-tetrahydrobenzoic acid butyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-1-methyl-tetrahydrobenzoic acid decyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-6-methyl-tetrahydrobenzoic acid ethyl ester, the product formed by reaction of dithiophosphoric acid-O,O-diethyl ester with 2,5-endomethylene-tetrahydrobenzyl alcohol, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with the Diels-Alder adduct of cyclopentadiene and allyl alcohol (2 mols:1 mol), the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with 2,5-endomethylene-tetrahydrophenyl acetate, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with the Diels-Alder adduct of cyclopentadiene and vinyl acetate (2 mols:1 mol), the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with the bis-cyclopentadiene adduct of p-benzoquinone, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with the azodicarboxylic acid diethyl ester, the product formed by reaction of dithiophosphoric acid-O,O-dimethyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-dibutyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-diethyl ester with dicyclopentadiene, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with wax olefin, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with oleyl alcohol, the product formed by reaction of dithiophosphoric acid-O,O-di-2-ethylhexyl ester with linseed oil, the product formed by reaction of dithiophosphoric acid-O,O-diamyl ester with alpha pinene, the product formed by reaction of dithiophosphoric acid-O,O-diphenyl ester with alpha pinene, the product formed by reaction of dithiophosphoric acid-O,O-diamyl ester with allo-ocimene, the product formed by reaction of dithiophosphoric acid-O,O-diisopropyl ester with styrene, propene, isobutene, 1-octene, methylcyclohexene, butadiene, isoprene, dipentene, etc., and the like.

#### Demulsifiers.

Typical additives which may be employed as demulsifiers include alkyl benzene sulphonates, polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, salts and esters or oil soluble acids, and the like.

Thus, for example use can be made of oxyalkylated trimethylol alkanes with molecular weights in the range of 1,000 to 10,000, and preferably in the range of 3,000 to 8,000. Preferably, the oxyalkylated trimethylol alkane is an oxyalkylated trimethylol ethane or propane, especially where the oxyalkylene groups are composed of a mixture of propyleneoxy and ethyleneoxy groups and where these groups are so disposed as to form relatively hydrophobic blocks adjacent the trimethylol group and relatively hydrophilic blocks remote the trimethylol group. Typical oxyalkylated trimethylol propane demulsifiers are described in U.S. Pat. No. 3,101,374. Commercially available products of this type are available from BASF Corporation under the Pluradot trademark. They are available in various molecular weights. Pluradot HA-510 has an average molecular weight of 4,600 and Pluradot HA-530 has an average molecular weight of about 5,300. Pluradot additives are propoxylated and ethoxylated trimethylol propanes.

Another type of suitable demulsifiers are oxyalkylated alkyl phenol-formaldehyde condensation products. Typically, these products have molecular weights in the range of about 4,000 to about 6,000 and are comprised of lower alkyl substituted phenol moieties joined together by methylene groups and in which the hydroxyl groups of the phenolic moieties have been ethoxylated. One such commercial product is marketed by Ceca S.A. of Paris, France under the "Prochinor GR77" trade name. The product is supplied as a concentrate in an aromatic solvent and the active ingredient is believed to be an ethoxylated nonylphenol-formaldehyde condensate of molecular weight 4,200 (by gel permeation chromatography calibrated with polystyrene).

Another suitable type of demulsifier is comprised of the tetra-polyoxyalkylene derivatives of ethylene diamine,

especially the tetra-poly(oxyethylene)-poly(oxypropylene) derivatives of ethylene diamine. Materials of this type are available commercially from BASF Corporation under the "Tetronics" trademark. Materials of this general type are described in U.S. Pat. No. 2,979,528.

Mixtures of alkylaryl sulphonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Petrolite Corporation under the TOLAD trademark, are also suitable. One such proprietary product, identified as TOLAD 286K, is understood to be a mixture of these components dissolved in a solvent composed of alkyl benzenes. TOLAD 286 is believed to be a similar product wherein the solvent is composed of a mixture of heavy aromatic naphtha and isopropyl alcohol.

Preferred demulsifiers are proprietary materials available from BASF Corporation under the Pluronic trademark. These are block copolymers of propylene oxide and ethylene oxide.

#### Copper corrosion inhibitors.

One type of such additives is comprised of thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,749,311; 2,760,933; 2,765,289; 2,850,453; 2,910,439; 3,663,561; 3,862,798; 3,840,549; and 4,097,387.

Other suitable inhibitors of copper corrosion include ether amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

#### Other Additive Components.

The oleaginous fluids and additive concentrates of this invention can and preferably will contain additional components in order to partake of the properties which can be conferred to the overall composition by such additional components. The nature of such components will, to a large extent, be governed by the particular use to which the ultimate oleaginous composition (lubricant or functional fluid) is to be subjected. Some of these other additives are referred to below.

A) Other phosphorus-containing antiwear and/or extreme pressure agents. As noted above, oil-soluble phosphorus- and nitrogen-containing compounds are the preferred antiwear and/ or extreme pressure agents for use in the compositions of this invention. However, metal-free phosphorus-containing compounds which do not contain nitrogen can be used either in lieu of or in addition to the phosphorus- and nitrogen-containing antiwear and/or extreme pressure agents described above. Such nitrogen-free compounds are for the most part partially or fully esterified acids of phosphorus, and include for example oil-soluble phosphates, phosphites, phosphonates, phosphonites, and their various sulphur analogs.

B) Supplemental ashless dispersants. Any of a variety of additional ashless dispersants can be utilized in the compositions of this invention. These include carboxylic ashless dispersants, polymeric polyamine dispersants, and post-treated dispersants of these types.

The carboxylic ashless dispersants are reaction products of an acylating agent (e.g., a monocarboxylic acid, dicarboxylic acid or other polycarboxylic acid, or derivatives thereof) with one or more polyamines and/or polyhydroxy compounds. These products, are described in many patents, including British Patent Specification 1,306,529 and the following U. S. Patents: 3,163,603; 3,184,474; 3,215,707; 3,219,666; 3,271,310; 3,272,746; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,340,281; 3,341,542; 3,346,493; 3,381,022; 3,399,141; 3,415,750; 3,433,744; 3,444,170; 3,448,048; 3,448,049; 3,451,933; 3,454,607; 3,467,668; 3,522,179; 3,541,012; 3,542,678; 3,574,101; 3,576,743; 3,630,904; 3,632,510; 3,632,511; 3,697,428; 3,725,441; 3,868,330; 3,948,800; 4,234,435 and Re 26,433.

There are a number of sub-categories of carboxylic ashless dispersants. One such sub-category which constitutes a preferred type is composed of the polyamine succinamides and more preferably the polyamine succinimides in which the succinic group contains a hydrocarbyl substituent, usually an alkenyl substituent, containing at least 30 carbon atoms. These dispersants are usually formed by reacting a polyamine with an alkenyl succinic acid or anhydride such as a polyisobutenyl succinic acid and anhydride wherein the polyisobutenyl group has a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and typically in the range of 800 to 1,300. The polyamine used in forming such compounds contains at least one primary amino group capable of forming an imide group on reaction with a hydrocarbon-substituted succinic acid or acid derivative thereof such an anhydride, lower alkyl ester, acid halide, or acid-ester. The literature is replete with descriptions of polyamines suitable for use in



forming such carboxylic ashless dispersants. See for example U.S. Pat. No. 5,034,018 which describes not only simple polyamines but amido-amine adducts which are suitable for use in forming such carboxylic ashless dispersants. Representative examples of such dispersants are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; 4,234,435; and 5,034,018. As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between the amine reactant(s) and the hydrocarbon-substituted carboxylic acid or anhydride (or like acid derivative) reactant(s), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Another sub-category of carboxylic ashless dispersants which can be used in the compositions of this invention includes alkenyl succinic acid esters and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C<sub>1</sub>-C<sub>4</sub>) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydrides can be merely reacted with an appropriate alkylene oxide such as ethylene oxide, propylene oxide, and the like, including mixtures thereof.

Still another sub-category of carboxylic ashless dispersants useful in forming compositions of this invention comprises an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters or etc. with an alcohol and an amine either sequentially or in a mixture. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 1-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms.

The polymeric polyamine dispersants are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials include, but are not limited to, interpolymers of decyl methacrylate, vinyl decyl ether or a relatively high molecular weight olefin with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in the following patents: U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

The various ashless dispersants referred to above can be subjected to post-treatment with one or more suitable reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, anhydrides of low molecular weight dibasic acids, nitriles, epoxides, phosphorus acids, phosphorus esters, boron compounds, and the like. Such post-treated ashless dispersants can be used in forming the compositions of this invention. Examples of post-treatment procedures and post-treated ashless dispersants are set forth in the following U.S. Patents: U.S. Pat. Nos. 3,036,003; 3,200,107; 3,216,936; 3,256,185; 3,278,550; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,702,757; and 3,708,522; and 4,971,598.

Mannich-based derivatives of hydroxyaryl succinimides that have been post-treated with C<sub>5</sub>-C<sub>9</sub> lactones such as ε-caprolactone and optionally with other post-treating agents as described for example in U.S. Pat. No. 4,971,711 can also be utilized. See also related U.S. Pat. Nos. 4,820,432; 4,828,742; 4,866,135; 4,866,139; 4,866,140; 4,866,141; 4,866,142; 4,906,394; and 4,913,830 for other similar materials.

**C) Antioxidants.** Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulphurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one bis(4-alkylphenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

**D) Rust inhibitors.** The compositions of this invention may also contain a suitable quantity of a rust inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces.

**E) Antifoam agents.** Suitable antifoam agents include silicones and organic polymers such as acrylate polymers. Various antifoam agents are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176).

**F) Friction modifiers.** These materials include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat. 4,105,571, oleamide, and the like. Such additives, when used are generally present in amounts of 0.1 to 5 weight percent. Glycerol oleates

are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

G) Seal swell agents. Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions.

H) Viscosity index improvers. Depending upon the viscosity grade required, the lubricant compositions can contain one or more viscosity index improvers (polymeric materials which are often supplied in the form of a solution in a solvent or carrier fluid).

Dispersant viscosity index improvers, which combine the activity of dispersants and viscosity index improvers, suitable for use in the compositions of this invention are described, for example, in U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; 4,519,929; 5,035,819; 5,035,820; 5,035,821; and 5,035,822.

When using a viscosity index improver or a dispersant viscosity index improver it is preferred to use a material which exhibits high shear stability as measured by the FZG or Kurt-Orbahn shear stability rigs.

I) Pour point depressants. Another useful type of additive which can be included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715.

J) Other metal corrosion inhibitors. In order to protect such metals as lead, cadmium, aluminum, magnesium, silver, zinc and alloys thereof, etc., special corrosion inhibitors can be used. These include such substances as gallic acid esters, phthalic acid esters, and the like.

The above descriptions (A through J inclusive) of other additives which can be used in the compositions of this invention is not to be construed as limitative, as many other types of additives can be used in such compositions. The only requirements are that such other additives not excessively interfere adversely with the performance of the compositions of this invention and that they exhibit suitable compatibility with the additives otherwise being employed therein.

#### Base oils.

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly- $\alpha$ -olefins (e.g., hydrogenated or unhydrogenated  $\alpha$ -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and inter-polymers of  $C_2$ - $C_{12}$  olefins, carboxylic acid esters of both monoalcohols

and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C<sub>2</sub>-C<sub>12</sub> monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils.

Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C<sub>6</sub>-C<sub>16</sub>  $\alpha$ -olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, e.g., under the trade designations ETHYL-FLO 162, ETHYL-FLO 164, ETHYL-FLO 166, ETHYL-FLO 168, ETHYL-FLO 170, ETHYL-FLO 174, and ETHYL-FLO 180 poly- $\alpha$ -olefin oils (Ethyl Corporation; Ethyl Canada Limited; Ethyl S.A.). Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C<sub>1-20</sub> alcohol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

For some applications, for example use under conditions where oxidative or thermal degradation of the base oil is unlikely to be experienced, unhydrogenated 1-alkene oligomers can be used as the base oil or as a component in a base oil blend.

Likewise, various proprietary synthetic lubricants such as KETJENLUBE synthetic oil of Akzo Chemicals can be employed either as the sole base lubricant or as a component of the base lubricating oil.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as biodegradability, high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

#### Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. When employing free amine, the amount employed is most preferably the amount sufficient to render the pH (determined as described hereinafter) of the finished additive concentrate as formed within the range of 6 to 8. The amounts of the other components will vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, the following concentrations (weight percent) of the components (active ingredients, i.e., excluding diluents which often are associated therewith) in the base oils or fluids are illustrative:

	Typical Range	Preferred Range
Mannich base	0.1 - 3	0.2 - 2
S-contg antiwear/E.P. agent	0.1 - 6	1 - 4

(continued)

	Typical Range	Preferred Range
P-contg antiwear/E.P. agent	0.1 - 3	0.1 - 2
Amine salt of carboxylic acid	0 - 1	0.01 - 2
Free amine	0 - 2	0 - 1
Trihydrocarbyl dithiophosphate	0 - 3	0 - 2
Demulsifier	0 - 1	0 - 0.2
Cu corrosion inhibitor	0 - 0.5	0.01 - 0.2
Other P-antiwear/E.P. agent	0 - 0.7	0.05 - 0.4
Supplemental ashless dispersant	0 - 3	0 - 2
Antioxidant	0 - 2	0 - 1
Supplemental Rust inhibitor	0 - 2	0.02 - 1
Antifoam agent	0 - 0.3	0.0002 - 0.1
Friction modifier	0 - 3	0 - 1
Seal swell agent	0 - 20	0 - 10
Viscosity index improver	0 - 20	0 - 15
Pour point depressant	0 - 2	0 - 1
Other metal corrosion inhibitors	0 - 1	0 - 0.5

It is to be noted that some additives are multifunctional additives capable of contributing more than a single property to the blend in which they are used. Thus when employing a multifunctional additive component in the compositions of this invention, the amount used should of course be sufficient to achieve the function(s) and result(s) desired therefrom.

It will be appreciated that the individual components can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which in many instances are blended apart from other components), it is preferable to blend the other selected components into the base oil by use of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

The additive concentrates of this invention will contain the individual components in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 80% by weight of one or more diluents or solvents can be used.

The oleaginous liquids provided by this invention can be used in a variety of applications. For example, they can be employed as crankcase lubricants, gear oils, hydraulic fluids, manual transmission fluids, automatic transmission fluids, cutting and machining fluids, brake fluids, shock absorber fluids, heat transfer fluids, quenching oils, transformer oils, and the like. The compositions are particularly suitable for use as automotive and industrial gear oils.

#### Blending

To make the compositions of this invention, one either purchases or synthesizes each of the respective individual components to be used in the formulation or blending operation. Unless one is already in the commercial manufacture of one or more such components, it is usually simpler and thus preferable to purchase, to the extent possible, the ingredients to be used in the compositions of this invention. If it is desired to synthesize one or more components, use may be made of synthesis procedures referred to in the literature, including, but by no means limited to, the applicable references cited herein. In some cases, the components can be formed in situ by in situ reactions between or among components introduced into the mixture. For example, amine salts of monothiophosphoric acid esters can be formed in situ by introducing into the blending vessel a material such as sulphurized isobutylene and one or more amines, followed by the introduction of one or more dihydrocarbyl hydrogen phosphites.

The formulation or blending operations are relatively simple and involve mixing together in a suitable container or vessel, using a dry, inert atmosphere where necessary or desirable, appropriate proportions of the selected ingredients. Those skilled in the art are cognizant of and familiar with the procedures suitable for formulating and blending additive concentrates and lubricant compositions. Usually the order of addition of components to the blending tank or vessel is not critical provided of course, that the components being blended at any given time are not incompatible or exces-

sively reactive with each other. Agitation such as with mechanical stirring equipment is desirable to facilitate the blending operation. Frequently it is helpful to apply sufficient heat to the blending vessel during or after the introduction of the ingredients thereto, so as to maintain the temperature at, say, 40-60°C, and preferably no higher than about 60°C. Similarly, it is sometimes helpful to preheat highly viscous components to a suitable temperature even before they are introduced into the blending vessel in order to render them more fluid and thereby facilitate their introduction into the blending vessel and render the resultant mixture easier to stir or blend. Naturally the temperatures used during the blending operations should be controlled so as not to cause any significant amount of thermal degradation or unwanted chemical interactions.

When forming the lubricant compositions of this invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achievement of product uniformity.

The following examples illustrate preferred additive concentrates and oleaginous compositions containing such concentrates. These examples are not intended to limit, and should not be construed as limiting, this invention.

#### EXAMPLE 1

To a reaction vessel are charged 38.0 parts of sulphurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of Primene® 81-R amine (a tert-alkyl primary amine mixture in the C<sub>12</sub>-C<sub>14</sub> range; Rohm & Haas), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of M530 defoamer (an antifoam concentrate of Monsanto Company) are added. Then, in a final stage and without application of heat, 1.8 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of Amoco 9250 additive (a proprietary product of Amoco Corporation, which is believed to be a 48% oil concentrate of boronated Mannich base ashless dispersant and which contains about 1.1% nitrogen and about 0.2% boron), 0.77 parts of Pluronic L-121 demulsifier (an ethylene oxide-propylene oxide block copolymer of BASF Corporation) and 10.83 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes. When dissolved in mineral oil at a concentration of 6.5 percent by weight, the finished GL-5 lubricant of this invention has a chlorine content of 20 ppm.

#### EXAMPLE 2

To a reaction vessel are charged 38.3 parts of sulphurized isobutylene, 14.3 parts of di-tert-nonyl polysulphide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of Primene 81-R amine, 3.7 parts of C<sub>16</sub> and C<sub>18</sub> primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 1 hour while maintaining the contents of the reaction vessel at 50°C. Then, while cooling the contents to 40°C, 0.6 part of C<sub>36</sub> dimer acid, 0.6 part of caprylic acid, 1.0 part of M530 defoamer, and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of Amoco 9250 additive, 0.5 part of Pluronic L-101 demulsifier (an ethylene oxide-propylene oxide block copolymer concentrate of BASF Corporation), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

#### EXAMPLE 3

To a reaction vessel are charged 35.8 parts of sulphurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C<sub>16</sub> and C<sub>18</sub> primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 1 hour while maintaining the contents of the reaction vessel at 50°C. Then while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of M544 defoamer (an acrylate copolymer concentrate of Monsanto Company), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of Amoco 9250 additive, 1.5 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole,

0.8 part of Chemax HCO-5 (a hydrogenated castor oil ethoxylate concentrate of Chemax, Inc.), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

#### 5 EXAMPLE 4

To a reaction vessel are charged 35.1 parts of sulphurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C<sub>16</sub> and C<sub>18</sub> primary amines, and 8.3 parts of process oil, and the mixture is stirred for 1 hour while maintaining the contents of the reaction vessel at 50°C. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of M544 defoamer, and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of Amoco 9250 additive, 1.3 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate of this invention is stirred for 60 minutes.

#### EXAMPLE 5

20 An SAE 80W-90 mineral oil blend of this invention is formed by blending together the following components in the amounts specified:

6.5% of the additive package of Example 1;

25 40.0% of high viscosity index 115 Solvent Neutral base oil (Shell Oil Company);

52.5% of high viscosity index 650b bright stock base oil (Shell Oil Company); and

1.0% of HiTEC® 623 additive; (an alkyl polymethacrylate pour point depressant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.)

#### EXAMPLE 6

35 An SAE 80W-90 mineral oil blend of this invention is formed by blending together the following components in the amounts specified:

3.2% of the additive package of Example 1;

95.8% of high viscosity index 115 Solvent Neutral base oil (Shell Oil Company);

40 1.0% of HiTEC® 623 additive.

#### EXAMPLE 7

45 A synthetic oil-based lubricating oil composition of this invention is formed by blending together the following components in the amounts specified:

6.5% of the additive package of Example 1;

50 39.9% of ETHYLFLO 168 poly- $\alpha$ -olefin oligomer oil (an 8 cSt base oil) (ETHYLFLO is a trademark of Ethyl Corporation);

43.6% of a low chlorine version of ETHYLFLO 174 poly- $\alpha$ -olefin oligomer oil (a 40 cSt base oil); and

55 10.0% of KETJENLUBE synthetic oil (KETJENLUBE is a trademark of Akzo Chemicals).

The procedure used in determining pH of preferred additive concentrates of this invention involves diluting the sample of the composition in a mixture of methanol and toluene and then assaying "non-aqueous" pH with a conven-

tional pH probe as used in aqueous systems. For this purpose, the basic equipment used is a potentiometer such as Beckman Zeromatic IV pH meter, Beckman Instruments Inc., available from CMS, catalog number 257-902, or equivalent; a glass indicating electrode 0-11 pH range, available from CMS, catalog number 39322 or equivalent; indicating electrode cable, available from Beckman Instruments Inc., catalog number 598979, or equivalent; saturated calomel reference electrode with ground glass sleeve junction, available from CMS, catalog number 39420, or equivalent; and reference electrode cable, available from Beckman Instruments Inc., catalog number 598982, or equivalent. The reagents used in this procedure are reagent grade toluene; potassium chloride; reagent grade methanol; buffer solution, pH 7.00, available from CMS, catalog number 061-622, or equivalent; buffer solution, pH 10.00, available from CMS, catalog number 061-648, or equivalent; and buffer solution, pH 4.00, available from CMS, catalog number 061-614, or equivalent. The steps used in the procedure are as follows:

- A. If the sample solution is expected to fall between the pH of 4.0 and 7.0, standardize the pH meter with these pH buffers. If the sample solution is expected to fall between the pH of 7.0 and 10.0, standardize the pH meter with these pH buffers. In standardizing with buffers standardize first with the buffer having a pH more remote from the suspected pH of the sample than the other buffer, and then use that other buffer.
- B. It is important to have a linear range over which the measurements are to be made. Therefore, repeat all of step A until no adjustments are needed in order to have a linear pH scale.
- C. Rinse the electrodes with distilled water, and blot dry with a clean, dry tissue.
- D. Using a top loading balance, weigh  $1.0 \pm 0.05$  g of sample into a 150-mL beaker.
- E. Add 50.0 mL by graduated cylinder of 1:1 volume of toluene and methanol. Alternatively, dissolve in 25.0 mL of toluene and then further dilute with 25.0 mL of methanol.
- F. Place a stirring bar into the beaker containing the sample and solvents and place on a magnetic stirrer.
- G. Insert the electrodes, turn on the pH meter, and stir for one minute.
- H. Record the pH to the nearest 0.05 pH unit.
- I. If recording more than one pH, rinse the electrodes with heptane, and with distilled water, and then blot dry with tissue, and then repeat steps F to H. When measurements have been completed, rinse the electrodes with distilled water and immerse them in a beaker of water for storage.

Copper corrosion ratings for the purposes of this invention are conducted using the standard ASTM D-130 procedure modified to the extent that the additive concentrate to be tested is first stored in an oven for 120 hours at 65°C. Then the concentrate is blended into the test oil to the selected test concentration and the test is conducted at 121°C.

As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration specified herein for use of such component. Preferably, however, the solubility of such component in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As is well known to those skilled in the art, certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions. Additives of this type can be employed in the compositions of this invention, provided they do not significantly interfere with the performance or usefulness of the composition in which they are employed.

The enhanced storage stability of the additive compositions of this invention was demonstrated in a series of storage tests. In these tests, an additive composition formed as in Example 1 was stored at ambient temperatures, in one case while in an open container exposed to the atmosphere and in another case, in an open container under conditions of high humidity. In neither case was a boric acid precipitate formed during storage periods of greater than 6 weeks. On the other hand, gear additive packages containing boronated succinimide such as Anglamol 6043B additive (The Lubrizol Corporation) gave noticeable boric acid precipitation after 2 days of storage under 100% relative humidity.

When subjected to the planetary gear test of the type described hereinabove, a typical composition of this invention was found to perform as well as the passing reference oil used by the original equipment manufacturer that developed the test procedure. Thus in duplicate tests in which the base oil was a mineral oil, the lubricant of this invention (Example 5) gave trouble-free operation for 75 to 80 hours under conditions where the mineral oil-based passing reference oil gave 70 to 75 hours of satisfactory performance. A synthetic oil-based lubricant of this invention (Example 7) was also subjected to the planetary gear test. In this case the composition of this invention gave trouble-free operation for 100 hours in the planetary spur gear test.

The effectiveness of the compositions of this invention in providing clean gear performance in the CRC L-60 test was shown in tests using lubricant compositions formed as in Examples 5 and 6. The results of such tests are summarized in the following table wherein the rating scale is from 1 to 10 in which 10 signifies no sludge deposit or varnish deposit as the case may be.

RESULTS OF CRC L-60 TESTS		
Composition Tested	Gear Rating, Sludge	Gear Rating, Varnish
Example 5	9.91	9.01
Example 6	9.95	8.71
Example 7	9.99	8.95

In other CRC L-60 tests a number of commercially available and experimental polyisobutene-based ashless dispersants were found to give inferior performance, particularly on the gear ratings for varnish. Of the various other polyisobutene-based ashless dispersant systems only an additive pack containing a boronated succinimide gave satisfactory results on gear varnish. However, the additive packages containing the boronated succinimide dispersant gave relatively poor demulsibility performance when subjected to the ASTM D1401 test procedure. In fact, in tests involving a large number of different demulsifier additives, including Pluronic L-121 used in Examples 5 and 6, it was not found possible to obtain good results for the boronated succinimide. In contrast, the composition of Example 5 was found to give good demulsibility performance in the ASTM D1401 test.

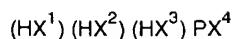
The lubricant compositions of this invention may be used in a wide variety of automotive and industrial gear applications. Examples of such applications include use in hypoid axles and in mechanical steering devices in passenger cars and in cross-country vehicles. Further examples include use in hypoid axles, planetary hub reaction axles, mechanical steering and transfer gear boxes in utility vehicles such as trucks.

Systems in which the lubricant compositions of this invention may additionally be used include pinion and planetary hub reduction gear boxes, synchromesh gear boxes, power take-off gears and limited slip rear axles, and synchroniser type gear boxes. The oleaginous compositions of this invention may also be used in transmission systems, including manual and automatic transmissions, and hydraulic systems operating under heavy loads and pressures. Vehicular crankcase usage is also possible using compositions of this invention. Other uses include cutting, shaping, and machining fluids, annealing fluids, transformer oils, and the like. The lubricants of this invention are of particular usefulness in gear oil applications.

#### Claims

1. An additive concentrate which comprises the following oil-soluble components:
  - a) a boronated Mannich base ashless dispersant;
  - b) a metal-free sulphur-containing antiwear and/or extreme pressure agent;
  - c) a metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
  - d) an oil-soluble amine salt of a carboxylic acid.
2. A concentrate as claimed in claim 1 wherein component c) is a metal-free phosphorus-containing and nitrogen-containing antiwear and/or extreme pressure agent.
3. A concentrate as claimed in claim 1 or 2 further comprising an oil-soluble trihydrocarbyl ester of a dithiophosphoric acid.
4. A concentrate as claimed in any one of claims 1 to 3 further comprising an oil-soluble demulsifying agent.
5. A concentrate as claimed in any one of claims 1 to 4 further comprise an oil-soluble copper corrosion inhibitor.
6. A concentrate as claimed in any one of claims 1 to 5 in which component b) comprises a sulphurised olefin.
7. A concentrate as claimed in any one of claims 1 to 6 in which component c) comprises:
  - (i) an amine salt of a monohydrocarbyl and/or dihydrocarbyl ester of a phosphoric or thiophosphoric acid of formula





in which  $X^1$ ,  $X^2$ ,  $X^3$  and  $X^4$  is, independently, an oxygen atom or a sulphur atom;

(ii) a phosphorus- and nitrogen-containing composition formed by reacting a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide to produce an acidic intermediate, and neutralizing at least a substantial portion of the acidic intermediate with an amine or hydroxyamine; and/or

(iii) an amine salt of a hydroxy-substituted phosphetane or hydroxythiophosphetane.

8. A concentrate as claimed in any one of claims 1 to 7 which comprises a component d) a mono-aliphatic monoamine salt of an aliphatic monocarboxylic acid.
9. A concentrate as claimed in any one of the claims 1 to 8 in which component a) comprises a boronated Mannich base ashless dispersant formed by reacting a long chain hydrocarbon-substituted phenol with formaldehyde and a polyalkylene polyamine, and boronating the resultant condensation product, component b) comprises sulphurised isobutylene, component c) comprises an amine salt of a monohydrocarbyl and/or dihydrocarbyl ester of a phosphoric and/or monothiophosphoric acid, and component d) comprises a tertiary alkyl primary monoamine salt of an aliphatic monocarboxylic acid.
10. A concentrate as claimed in claim 9 wherein the amine of components c) and d) comprise a tert-alkyl primary monoamine in which the alkyl group contains at least 10 carbon atoms.
11. A concentrate as claimed in any one of claims 1 to 10 comprising a diluent oil and at least 20% by weight of additive components a), b) and c) wherein the mass ratio (wt/wt) of nitrogen in a) to sulphur in b) is from 0.0005:1 to 0.5:1.
12. A concentrate as claimed in claim 11 wherein the mass ratio (wt/wt) of nitrogen a) to sulphur in b) is from 0.003:1 to 0.2:1.
13. A concentrate as claimed in any one of claims 1 to 12 comprising a diluent oil and at least 20% of additive components a), b) and c) wherein the mass ratio (wt/wt) of nitrogen in a) to phosphorus in c) is from 0.005:1 to 5:1.
14. A concentrate according to claim 13 wherein the mass ratio (wt/wt) of nitrogen in a) to phosphorus in c) is from 0.01:1 to 2:1.
15. A concentrate according to any one of claims 11 to 14 which includes as additional components an oil-soluble demulsifying agent and an oil-soluble copper corrosion inhibitor and wherein component c) is an oil-soluble amine salt of a dihydrocarbyl ester of a monothiophosphoric acid and an oil-soluble trihydrocarbyl ester of a dithiophosphoric acid.
16. An oleaginous composition which comprises an oil of lubricating viscosity and the oil-soluble additive components defined in any one of claims 1 to 14.
17. A composition according to claim 16 wherein the oil of lubricating viscosity comprises mineral lubricating oil.
18. A composition according to claim 16 wherein the oil of lubricating viscosity comprises poly- $\alpha$ -olefin synthetic lubricating oil.
19. A method of lubricating relatively moving metallic surfaces in close proximity to each other which comprises providing for use or using as the lubricant for such surfaces an oleaginous composition as defined in any one of claims 16 to 18.
20. A method according to claim 19 wherein the relatively moving metallic surfaces comprise surfaces of at least two interacting metallic gears that transfer mechanical energy during operation.
21. The combination of an apparatus comprising (i) metallic mechanical parts in close proximity to each other requiring lubrication, and (ii) as a lubricant therefor, an oleaginous composition as claimed in any one of claims 16 to 18.

22. The combination according to claim 21 wherein the apparatus comprises at least two interacting metallic gears that transfer mechanical energy during operation.

## 5 Patentansprüche

1. Additivkonzentrat, das die folgenden öllöslichen Bestandteile enthält:

- a) ein aschefreies Dispergiermittel in Form einer borierten Mannichbase;  
 b) ein metallfreies, schwefelhaltiges Antiverschleiß- und/oder Höchstdruckmittel;  
 c) ein metallfreies, phosphorhaltiges Antiverschleiß- und/oder Höchstdruckmittel sowie  
 d) ein öllösliches Aminsatz einer Carbonsäure.

2. Konzentrat nach Anspruch 1, worin der Bestandteil c) ein metallfreies, phosphorhaltiges und stickstoffhaltiges Antiverschleiß- und/oder Höchstdruckmittel darstellt.

3. Konzentrat nach Anspruch 1 oder 2, das zusätzlich noch einen öllöslichen Tri kohlwasserstoffester einer Dithio phosphorsäure enthält.

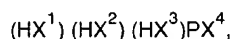
4. Konzentrat nach einem der Ansprüche 1 bis 3, das zusätzlich noch ein öllösliches emulsionsbrechendes Mittel enthält.

5. Konzentrat nach einem der Ansprüche 1 bis 4, das zusätzlich noch einen öllöslichen Kupferkorrosionsinhibitor enthält.

6. Konzentrat nach einem der Ansprüche 1 bis 5, worin der Bestandteil b) ein sulfuriertes Olefin enthält.

7. Konzentrat nach einem der Ansprüche 1 bis 6, worin der Bestandteil c) die folgenden Komponenten aufweist:

- (i) ein Aminsatz eines Monokohlwasserstoff- und/oder Dikohlwasserstoffesters einer Phosphor- oder Thiophosphorsäure der Formel



worin  $X^1$ ,  $X^2$ ,  $X^3$  und  $X^4$  unabhängig voneinander ein Sauerstoff- oder Schwefelatom bedeuten;

(ii) eine phosphor- und stickstoffhaltige Zusammensetzung, die durch die Reaktion eines hydroxysubstituierten Triesters einer Phosphorthiosäure mit einer anorganischen Phosphorsäure, einem Phosphoroxid oder Phosphorhalogenid zur Synthese eines sauren Zwischenproduktes und durch Neutralisation mindestens eines wesentlichen Anteils an dem sauren Zwischenprodukt mit einem Amin oder Hydroxyamin gebildet worden ist, und/oder

(iii) ein Aminsatz eines hydroxysubstituierten Phosphetans oder Hydroxythiophosphetans.

8. Konzentrat nach einem der Ansprüche 1 bis 7, worin der Bestandteil d) ein monoaliphatisches Monoaminsatz einer aliphatischen Monocarbonsäure aufweist.

9. Konzentrat nach einem der Ansprüche 1 bis 8, worin der Bestandteil a) ein aschefreies Dispergiermittel in Form einer borierten Mannichbase aufweist, das durch die Reaktion eines mit einem langkettigen kohlwasserstoff-substituierten Phenol mit einem Formaldehyd und einem Polyalkylenpolyamin sowie durch Borieren des so erhaltenen Kondensationsproduktes gebildet worden ist; der Bestandteil b) sulfuriertes Isobutylen; der Bestandteil c) ein Aminsatz eines Monokohlwasserstoff- und/oder Dikohlwasserstoffesters einer Phosphor- und/oder Monothiophosphorsäure, sowie der Bestandteil d) ein primäres tert.-Alkyl-Monoaminsatz einer aliphatischen Monocarbonsäure umfaßt.

10. Konzentrat nach Anspruch 9, worin das Amin gemäß den Bestandteilen c) und d) ein primäres tert.-Alkyl-Monoamin umfaßt, worin die Alkylgruppe mindestens 10 Kohlenstoffatome aufweist.

11. Konzentrat nach einem der Ansprüche 1 bis 10, das ein Verdünnungsöl und mindestens 20 Gew.-% an Additiv-

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bestandteilen a), b) und c) umfaßt, worin das Massenverhältnis (Gew./Gew.) von Stickstoff in a) zu Schwefel in b) 0,0005:1 bis 0,5:1 beträgt.

12. Konzentrat nach Anspruch 11, worin das Massenverhältnis (Gew./Gew.) von Stickstoff in a) zu Schwefel in b) 0,003:1 bis 0,2:1 beträgt.

13. Konzentrat nach einem der Ansprüche 1 bis 12, das ein Verdünnungsöl und mindestens 20% an Additivbestandteilen a), b) und c) umfaßt, worin das Massenverhältnis (Gew./Gew.) von Stickstoff in a) zum Phosphor in c) 0,005:1 bis 5:1 beträgt.

14. Konzentrat nach Anspruch 13, worin das Massenverhältnis (Gew./Gew.) von Stickstoff in a) zum Phosphor in c) 0,01:1 bis 2:1 beträgt.

15. Konzentrat nach einem der Ansprüche 11 bis 14, das als zusätzliche Bestandteile ein öllösliches emulsionsbrechendes Mittel sowie einen öllöslichen Kupferkorrosionsinhibitor mit einschließt, wobei darin der Bestandteil c) ein öllösliches Aminsalt eines Dikohlenwasserstoffesters einer Monothiophosphorsäure und einen öllöslichen Trikohlenwasserstoffester einer Dithiophosphorsäure darstellt.

16. Ölartige Zusammensetzung, die ein Öl von schmierender Viskosität und die öllöslichen Additivbestandteile umfaßt, wie sie in einem der Ansprüche 1 bis 14 definiert sind.

17. Zusammensetzung nach Anspruch 16, worin das Öl mit Schmiermittelviskosität ein mineralisches Schmieröl umfaßt.

18. Zusammensetzung nach Anspruch 16, worin das Öl mit Schmiermittelviskosität ein synthetisches Poly- $\alpha$ -olefin-Schmieröl umfaßt.

19. Verfahren zum Schmieren von metallischen, sich relativ zueinander bewegenden Oberflächen in enger Nachbarschaft zueinander, das die Bereitstellung für den Gebrauch oder die Verwendung als Schmiermittel für derartige Oberflächen in Form einer ölartigen Zusammensetzung gemäß Definition nach einem der Ansprüche 16 bis 18 umfaßt.

20. Verfahren nach Anspruch 19, worin die Metalloberflächen, die sich relativ zueinander bewegen, Oberflächen von mindestens 2 miteinander in Eingriff befindlichen Getriebezahnradern aus Metall umfassen, die mechanische Energie während des Betriebs übertragen.

21. Kombination aus einer apparativen Vorrichtung, die (i) metallische mechanische Bauteile in enger Nachbarschaft zueinander umfaßt, die das Abschmieren erforderlich machen, und (ii) einem Schmiermittel in Form einer ölartigen Zusammensetzung nach einem der Ansprüche 16 bis 18.

22. Kombination nach Anspruch 21, worin die apparative Vorrichtung mindestens zwei miteinander in Eingriff stehende Getriebezahnradern aus Metall umfaßt, die mechanische Energie während des Betriebs übertragen.

### Revendications

1. Concentré d'additifs comprenant les composants oléosolubles suivants :

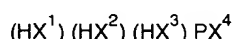
- a) un dispersant sans cendres formé d'une base de Mannich borée ;
- b) un agent anti-usure et/ou extrême pression contenant du soufre et exempt de métal ;
- c) un agent anti-usure et/ou extrême pression contenant du phosphore et exempt de métal ; et
- d) un sel aminé d'un acide carboxylique soluble dans l'huile.

2. Concentré selon la revendication 1, dans lequel le composant c) est un agent anti-usure et/ou extrême pression sans métal contenant du phosphore et contenant de l'azote.

3. Concentré selon la revendication 1 ou 2, comprenant, en outre, un ester oléosoluble de trihydrocarbyle et d'acide dithiophosphorique.

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4. Concentré selon l'une quelconque des revendications 1 à 3, comprenant, en outre, un agent désémulsifiant oléo-soluble.
- 5 5. Concentré selon l'une quelconque des revendications 1 à 4, comprenant, en outre, un inhibiteur de corrosion par le cuivre, qui est oléosoluble.
6. Concentré selon l'une quelconque des revendications 1 à 5, dans lequel le composant b) comprend une oléfine sulfurée.
- 10 7. Concentré selon l'une quelconque des revendications 1 à 6, dans lequel le composant c) comprend:  
(i) un sel aminé d'un ester de monohydrocarbyle et/ou de dihydrocarbyle et d'acide phosphorique ou thiophosphorique, répondant à la formule



où X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> et X<sup>4</sup> sont indépendamment les uns des autres un atome d'oxygène ou un atome de soufre ;  
(ii) une composition contenant du phosphore et de l'azote, formée par réaction d'un triester à substituant hydroxy d'acide phosphorothioïque avec un acide phosphoreux inorganique, un oxyde phosphoreux ou un halogénure phosphoreux pour produire un composé intermédiaire acide, et par neutralisation d'au moins une partie substantielle du composé intermédiaire acide avec une amine ou une hydroxyamine ; et/ou  
(iii) un sel aminé d'un phosphétane ou d'un hydroxythiophosphétane à substituant hydroxy.

- 25 8. Concentré selon l'une quelconque des revendications 1 à 7, comprenant en composant d) sel de monoamine monoaliphatique et d'un acide monocarboxylique aliphatique.
9. Concentré selon l'une quelconque des revendications 1 à 8, dans lequel le composant a) comprend un dispersant sans cendres formé d'une base de Mannich qui est formée par réaction d'un phénol substitué par un hydrocarbure à chaîne longue avec du formaldéhyde et une polyalkylène-polyamine, et par boration du produit de condensation résultant, le composant b) comprend de l'isobutylène sulfuré, le composant c) comprend un sel aminé d'un ester de monohydrocarbyle et/ou de dihydrocarbyle et d'acide phosphorique et/ou monothiophosphorique, et le composant d) comprend un sel d'une monoamine primaire d'alkyle tertiaire et d'un acide monocarboxylique aliphatique.
- 30 10. Concentré selon la revendication 9, dans lequel l'amine des composants c) et d) comprend une monoamine primaire de tert-alkyle dans laquelle le groupe alkyle contient au moins 10 atomes de carbone.
11. Concentré selon l'une quelconque des revendications 1 à 10, comprenant une huile diluante et au moins 20 % en poids de composants additifs a), b) et c), dans lequel le rapport en masse (poids/poids) de l'azote dans a) au soufre dans b) est de 0,0005:1 à 0,5:1.
- 40 12. Concentré selon la revendication 11, dans lequel le rapport en masse (poids/poids) de l'azote dans a) au soufre dans b) est de 0,003:1 à 0,2:1.
- 45 13. Concentré selon l'une quelconque des revendications 1 à 12, comprenant une huile diluante et au moins 20 % de composants additifs a), b) et c), dans lequel le rapport en masse (poids/poids) de l'azote dans a) au phosphore dans c) est de 0,005:1 à 5:1.
- 50 14. Concentré selon la revendication 13, dans lequel le rapport en masse (poids/poids) de l'azote dans a) au phosphore dans c) est de 0,01:1 à 2:1.
15. Concentré selon l'une quelconque des revendications 11 à 14, comprenant, comme composants supplémentaires, un agent désémulsifiant oléosoluble et un inhibiteur de corrosion par le cuivre, qui est oléosoluble, et dans lequel le composant c) est un sel aminé oléosoluble d'un ester de dihydrocarbyle et d'acide monothiophosphorique et d'un ester oléosoluble de trihydrocarbyle et d'acide dithiophosphorique.
- 55 16. Composition oléagineuse comprenant une huile de viscosité lubrifiante et les composants additifs oléosolubles définis dans l'une quelconque des revendications 1 à 14.

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17. Composition selon la revendication 16, dans laquelle l'huile de viscosité lubrifiante comprend une huile minérale lubrifiante.
- 5 18. Composition selon la revendication 16, dans laquelle l'huile de viscosité lubrifiante comprend une huile lubrifiante synthétique poly- $\alpha$ -oléfinique.
- 10 19. Procédé de lubrification de surfaces métalliques mobiles très proches l'une de l'autre, comprenant la mise à disposition ou l'utilisation d'une composition oléagineuse telle que définie dans l'une quelconque des revendications 16 à 18 comme lubrifiant pour de telles surfaces.
20. Procédé selon la revendication 19, dans laquelle les surfaces métalliques relativement mobiles comprennent les surfaces d'au moins deux engrenages métalliques en interaction qui transfèrent une énergie mécanique pendant le fonctionnement.
- 15 21. Combinaison d'un appareil comprenant (i) des pièces mécaniques métalliques très proches les unes des autres, nécessitant une lubrification, et (ii) une composition oléagineuse selon l'une quelconque des revendications 16 à 18 comme lubrifiant pour celles-ci.
- 20 22. Combinaison selon la revendication 21, dans laquelle l'appareil comprend au moins deux engrenages métalliques en interaction qui transfèrent une énergie mécanique pendant le fonctionnement.